14p

[redacted]

SPECTROSCOPY AND SOLID STATE QUANTUM ELECTRONICS AT OPTICAL AND INFRARED WAVELENGTHS

under the direction of

A.L. Schawlow

Semi-Annual Status Report No. 3

for

NASA Research Grant NsG-331
National Aeronautics and Space Administration
Washington 25, D. C.

UNPUBLISHED PRELIMINARY DATA

for the period

October 1, 1963 to March 31, 1964

M. L. Report No. 1163

May 1964

Microwave Laboratory
W. W. Hansen Laboratories of Physics
Stanford University
Stanford, California

[redacted]

RC
#3

STAFF

NASA Research Grant NsG-331
for the period
1 October 1963 to 31 March 1964

PRINCIPAL INVESTIGATOR

A. L. Schawlow, Professor

ASSISTANT PROFESSOR

H. W. Moos

RESEARCH ASSOCIATES

H. G. Freie
W. M. Yen

RESEARCH ASSISTANTS

M. Berggren
J.L. Emmett
R. L. Greene
S. A. Johnson
B. McCaul
L.F. Mollenauer
E. D. Nelson
J. L. Rapier
W. C. Scott
R. A. Soref
W. B. Tiffany

[redacted]

INTRODUCTION

This program is concerned with the properties of infrared and optical masers, with their scientific applications, and with related materials problems. These areas complement each other, in that new knowledge of materials makes possible improvements in devices, and improved devices make possible new kinds of experiments.

Several talks have been given during this period, embodying results obtained under this grant:

(1) J. L. Emmett, A. L. Schawlow and E. H. Weinberg (Office of Naval Research), "Direct Measurement of Xenon Flashtube Opacity," Conference on Flash Lamps for Laser Pumping, at Stanford Research Institute, Feb. 20, 1964.

(2) W. M. Yen and W. C. Scott, "Phonon-Induced Relaxation in Optically Excited States of LaF_3Pr^{3+}," American Physical Society, Philadelphia, March 26, 1964 (paper JF 12).

(3) H. W. Moos, "Optical Harmonic Generation in Semiconductors," Johns Hopkins University, Baltimore, November 4, 1963.

(4) H. W. Moos, "Optical Harmonic Generation in Semiconductors," University of Minnesota, February 5, 1964.

Two papers have been accepted for publication, and will appear in the Journal of Applied Physics:

(1) J. L. Emmett, A. L. Schawlow and E. H. Weinberg, "Direct Measurement of Xenon Flashtube Opacity."

(2) R. A. Soref and H. W. Moos; "Optical Second Harmonic Generation In ZnS-CdS and CdS - CdSe Alloys."

R. A. Soref received the Ph.D degree in Electrical Engineering during this period. His work was partly supported by this grant. The title of his dissertation is "Optical Second-Harmonic Generation in Semiconductor Alloys."

PRESENT STATUS

1. <u>High Intensity Pulsed Lasers</u> (J. L. Emmett, R. L. Greene, S. Johnson, W. M. Yen)

(a) Properties of Flashtubes for Laser Pumping

Since the last progress report an investigation has been initiated into the question of the optical opacity of a flashtube. It is important, in the design of high power laser pump configurations to know how transparent the flashtube is to its own radiation, particularly in the pump bands of the laser material being used. Also there has been much interest in doping standard flashtubes with various metal vapors to enhance the radiation in certain portions of the spectrum. If the flashtube, prior to doping, was already opaque in the region of the spectrum being considered, one could not expect an improvement in light output through doping. These considerations have led us to undertake the measurement of opacity of a standard Xenon flashtube from 2500 - 10,000 Å at current densities up to 5000 Amperes/cm^2.

This work has been completed and submitted for publication. It is found that the absorption increases with current and with wavelength. Above about 5000 Å and a current of 4000 amperes per cm^2, a discharge tube 1 cm thick is nearly opaque. At shorter wavelengths or lower currents, the discharge is fairly transparent.

(b) Construction of High-power Laser

The construction of the very high peak power laser is continuing and should be completed within the next period. The oscillator-amplifier concept is being used in this design. Two 3" x 1/2" diameter Brewster angle rubies are operated as a Q-switched oscillator. The oscillation output is then fed into several similar highly pumped rubies as amplifiers. Present construction allows the use of three 3" amplifier sections in addition to the two sections which comprise the oscillator. The ruby rods are pumped with two improved flashtubes in a close coupled configuration.

Arcs are continuously maintained in the flashtubes at a low current (50 mA) to remove the necessity of a high voltage trigger. This also allows all flashtubes in the system to be pulsed simultaneously (within 1 μsec). It will be possible to use almost all of the various Q-switching techniques including kerr cells, rotating mirrors, dye films or solutions, etc. It is presently planned to use a kerr cell, as it is the only device which allows jitter to be held in the range of 1-5 nanoseconds.

(c) Q-Spoil, Low-temperature Devices

Work has continued on a versatile Q-spoiled ruby laser which can be operated in the temperature range of $4.2^{\circ}K$ to room temperature. Certain cavity design changes were necessary to improve the threshold conditions; so that, with an unsilvered ruby rod stimulated emission was observed (at $77^{\circ}K$) at a ~ 300 joule energy threshold. During this period, we have built a rotating Q-spoil prism which is driven mechanically by a synchronous induction motor, and is capable of rotation speeds and stability superior to commercially available units. Incorporation of this Q-spoiling device into our Dewar,laser cavity, etc., system is now in progress.

Certain changes in the cavity and rod geometries, i.e., Brewster windows, etc., were also found to be necessary in order to prevent uncontrolled oscillations at high inversions.

Though it now appears that the experimental attainment of the optical analogy of NMR spin echoes is improbably due to radiation damping losses, studies of the homogeneous widths of ruby ^{2}E levels are still being planned. Plans are also being considered to study the transient behavior of the absorption coefficient of the ^{2}E levels as a function of saturation of, or pump power into, these levels.

2. Selective Photocatalysis of Chemical Reactions (H.W. Moos, W. Tiffany)

As described in the previous Status Reports, an investigation of the possibility of using a ruby optical maser to separate the isotopes of bromine is under way.

The spectra of isotopically pure samples of Br_2^{79} and Br_2^{81} have been examined in the region near 6940 Å, and compared with that of ordinary bromine (50% $Br^{79} Br^{81}$, 25% Br_2^{79} and Br_2^{81}). Several sharp lines belonging to the pure isotopes have been identified in the spectrum of ordinary Br_2. It is planned to excite a line of Br_2^{79} near 6939 Å which will require a ruby laser temperature of about - 40°C.

A ruby laser which is tunable by means of temperature and which can produce pulses of one joule at a maximum rate of about one a second has been constructed. The total width of the output for a pulse of about 0.5 joule is 0.25 cm^{-1}. The cooling system consists only of cooled gaseous N_2, but has a stability such that a superposition of some 0.500 shots on a Fabry-Perot interferometer showed a line width on the order of 1/3 cm^{-1}.

The isotope shift of the vibrational band heads of transitions to the $^3\Pi_1$ state was measured. From this, it was determined that the previous vibrational number assignment, which was not considered definite, is correct except that the published v' numbers should be reduced by 1.

3. Spectra of Exchange-Coupled Pairs of Ions in Ruby (L.F. Mollenauer)

During the past quarter we have made a detailed study of the splitting with uni-axial stress of the 7009 Å (N_2) and 7040 Å (N_1) lines in two sets of fully oriented dark ruby samples. The first set, of 3 samples, had all sample axes normal to C_3 and in the sequence parallel, perpendicular, and at 45° to C_2. The second set, cut from a slab whose large faces were parallel to a mirror plane, consisted of a fan of approximately 19 samples, whose axes were inclined at various angles to the C_3 axis, such as to cover the complete 180° range thus possible in 10° steps. For all but a few of the sample orientations, it has been possible to obtain two- or three-fold splittings, where the splittings are at least several times the widths of the individual components.

If we consider the first 6 nearest neighbor types as the only reasonable candidates for the production of the N lines, then the two- and three-fold splittings mentioned above immediately rule out first and fifth nearest neighbors, as there exists only one equivalent pair type for either of these two. The splittings can occur only for neighbor types where the point group symmetry operators of the crystal normally produce equivalent pair types, since it is then possible for an applied stress to make non-equivalent pair types by its destruction of one or more of the crystal symmetries. Of the four remaining neighbor types, all except the sixth have their pair axes lying in a mirror plane. A plot of the shift from the position for zero stress of one of the components of the split N_2 line, for a constant stress, versus the angle of the sample axis (for the mirror plane set), shows a sinusoidal curve with a maximum very near the angle, corresponding to the fourth nearest neighbor pair axis direction. If one makes the simplest and rather reasonable assumption that a pair line will undergo maximum shift when the pressure axis coincides with the pair axis, the above should constitute strong evidence for associating the N_2 line with the fourth nearest neighbors, especially when one considers that the other two possible types, second and third nearest neighbors, have pair axes that lie at radically different angles from that of the fourth nearest neighbor pairs.

We hope to substantiate the above by doing an accurate polarization study of the pressure-split components of the N_2 line. Our data indicate that the N_2 line is polarized along the fourth neighbor pair axis. However, to prove this, we need to use a sample cut from ruby of considerably higher optical quality than that available at the time we cut the above set of samples. We have recently received a boule of dark ruby from the Linde Company which we hope will be of the desired quality. The orientation and cutting of samples from this boule should be completed in a few weeks.

The work of Kapalyanski and Prizhuvskii has shown that the axis of the pair type associated with the N_1 line must be approximately in the plane to which C_3 is the normal. The only two candidates here are sixth and second nearest neighbors. Although there are rather strong theoretical grounds for choosing the latter of the two pair types, the theory of superexchange is sufficiently uncertain to make an independent experimental verification highly desirable.

Our stress data has verified and extended Kapalyanskii and Prizhuvskii's work, but at this time we are unable to offer as unambiguous an interpretation as was possible for the N_2 line. Further work with samples cut from our new ruby boule may enable us to answer this question in a definitive manner.

We are also very close to successful operation of a laser using dark ruby rods, which should allow maser action in the N_1 and N_2 lines before the threshold for maser action in the R line is reached. We will then use this N line laser to selectively excite the upper levels associated with the N_1 and N_2 lines in a second piece of dark ruby. The fluorescence of the dark ruby thus excited should show just four lines for each N line excited, and hence reveal in a very simple and unambiguous manner the exact exchange coupling parameters for the ground states of the two pair types. Previous attempts by other investigators to obtain this information have led to uncertain and sometimes conflicting results. The selective excitation method has never been tried before with the N lines of ruby because the extremely low absorption in these lines would make the experiment impossibly difficult with a standard light source and monochromator. Thus the N line laser will be a vital part of our experiment.

4. Spectra of Rare Earth Ions (H. Freie, W.C. Scott, W.M. Yen)

Studies of the temperature dependence of widths and positions of the optical spectra of some rare earth ions have been completed. We have concentrated our efforts on LaF_3: Pr^{3+} since recent work has shown it to be a promising laser material.

We have extended a theory on the temperature dependence of the widths which should apply to rare earth earth ion spectra in general. The several phonon relaxation processes commonly encountered in electron spin reasonance experiments in solids are proposed and investigated as the mechanisms responsible for the widths and and shifts observed in the sharp optical transitions of LaF_3: Pr^{3+}.

We have investigated, in particular, the linewidths of the transitions from the metastable $^3P_0$ state to the $^3H_4$, $^3H_6$, $^3F_2$ and $^3F_4$ states of LaF_3: Pr^{3+} as a function of temperature (0^o to 300^oK) and find them qualitatively and quantitatively explainable in terms of lifetime broadening of the terminal states by nonradiative (phonon) processes. Because of the complicated nature of the impurity ion sites of Pr^{3+} in LaF_3 and the non-Debye nature of the phonon density of states, values of the matrix elements between crystalline states cannot be accurately calculated. Instead, they are directly inferred from the zero temperature linewidths and other semi-empirical coefficients. With a few empirical coefficients for the Raman and direct phonon relaxation processes, the line width versus temperature curves are fitted closely over a wide range of temperatures.

Other phonon-ion interaction effects, such as line shifts and vibrational sidebands of rare earth ions in crystal lattices, are also investigated.

Results for LaF_3: Pr^{3+} are now in manuscript form and will soon be submitted for publication.

Investigation is continuing in Kramer's degenerate ions such as Er^{3+} in LaF_3 to further correlate results of optical studies with electron spin resonance studies. Line shifts are also being investigated to ascertain the correctness of second-order phonon-ion effects in these ions.

5. Optical Studies of Lattice Vibrations (W. C. Scott)

It is known that in crystals of Al_2O_3:V^{3+} the $^3A_2$ ground state is split by spin-orbit interaction into two levels which are separated by $7.8\ cm^{-1}$. Broadband absorption from this ground state to levels at $\approx 16,000\ cm^{-1}$ has been observed [M.H.L. Pryce and W. A. Runciman, Disc. Far. Soc. 26, 34 (1958)] which shows signs of partially resolved structure. It is planned to measure the absorption from each spin-orbit component of the ground state into this band by very low frequency modulation of the relative populations of these ground state levels together with phase-sensitive detection. The large thermal conductivity of the host crystal ($\approx$ 1 watt/cm-deg at 4.2K), together with the very small specific heat involved, allow this population modulation to be done by direct cycling of the sample temperature. The Boltzmann factor between the $m = \pm 1$ level and the $m = 0$ level is $\exp(-11.3/T)$.

The experiment will be performed on a sample placed in an evacuated and shielded absorption chamber with one end of the sample in direct contact with liquid helium and the other end attached to a heater. Cycling the heater current appropriately will then alternately "freeze out" and "thaw out" the population of the $m = \pm 1$ level.

Apparatus for this experiment is virtually complete. A satisfactory crystal has finally been obtained, and preliminary absorption measurements at static temperatures of 77°K, 20°K, and 4.2°K are being carried out at this writing.

6. Nonlinear Optical Effects in Solids (H. W. Moos and R. A. Soref)

Studies of optical harmonics, generated in various nonlinear semiconductors, have been completed. Specifically, optical second harmonic generation was measured as a function of alloy composition in wurtzite ZnS-CdS and CdS-CdSe monocrystals. A 1.06μ Nd^{3+} glass laser was used. The semiconductors have similar properties, but the band gaps decrease as a function of alloy composition from 3.5 eV for ZnS to 1.7 eV for CdSe. Thus, the nonlinear electric susceptibility should vary through the series in a manner analagous to the dispersion of the ordinary index of refraction. From the relative intensities of the harmonics and the published and measured values of the indices of refraction (the basic problem is that the fundamental and harmonic waves get out of phase, due to dispersion in the index of refraction and this must be corrected for) the relative values of the nonlinear electric susceptibilities were determined. The absolute value for CdS is in the literature so that the series is determined. It was found that the nonlinear susceptibility increased by almost one order of magnitude as the band gap was decreased from 1.52 ($2\hbar\omega$), ZnS, to 0.73 ($2\hbar\omega$), CdSe.

In fact, because of the strong increase in χ_{33}, appreciable second harmonic signals were detected in the crystals of the series which strongly absorbed at the harmonic frequency.

The above results agreed with a theoretical analysis using an idealized model of the semiconductors.

These semiconductors have similar properties, and to first order, it is felt that the change in the nonlinear electric susceptibilities is due to the change in band gap. Thus, the nonlinear part of the index of refraction has been demonstrated to increase as the photon energy approaches and exceeds the band gap. Studies of other II-VI and III-V compounds also indicate a similar strong dependence of the nonlinear susceptibilities upon the band gap.

A report on this work has been accepted for publication:("Optical Second Harmonic Generation in ZnS-CdS and CdS-CdSe Alloys," by R. A. Soref and H. W. Moos, to be published in J. Appl. Phys.).

7. Gas Discharge (Silver Vapor) Laser (J. Rapier)

The fused silica gas-laser tube, which will contain the silver vapor, is designed and half fabricated. The tubular furnace, which will serve to control the vapor pressure of the silver, is installed and ready to operate. The vacuum system, used to evacuate, and if necessary fill the laser tube with carrier gas, is present, but requires assembly and cleaning. The optical bench system for the end reflectors, etc.,is in the machine shop due to be finished at the end of April. The power supply for the electric discharge in the laser tube is in the initial design state.

It is anticipated that all the above components will be combined and that experimentation will begin within the next one to three months.

8. Far Infrared Spectroscopy (E. Nelson)

A large spectrograph for the far infrared region (initially 100 - 1000 microns) is under construction. A satisfactory vacuum tank has now been obtained and placed in position. A hand hoist has been installed, so that the upper half of the cylindrical tank can be lifted off. The tank's axis is horizontal, and the tank is split in a plane containing the axis.

In the next few months, the optical parts will be installed, and the spectrograph brought into operation. It will then be used, initially at least, for studies of energy levels of ions in crystals.

9. Transfer of Excitation Energy in Solids (H. G. Freie)

Some further measurements were made on terbium fluorescence in several crystals, and with various kinds of excitation. However, the results do not fit any evident simple pattern. It was decided, therefore, to put this project aside temporarily. When it is resumed, an attempt will be made to find a simple system so that individual energy transfer processes can be isolated.

10. Search for Nuclear Absorption Levels in the Optical Spectrum (B. McCaul)

This project considered the possibility of observing low-lying nuclear energy levels by an optical absorption technique. It was felt that in nuclear ground states there might well exist "fine structure" splittings having energy of 1.5 to 4 eV, corresponding roughly to the visual spectrum. This energy is a factor of 10^4 lower than the lowest rotational excitations of asymmetric nuclei, which are the lowest-lying common nuclear levels; there is one known instance of a nuclear excitation of the appropriate energy.

The interest of this group lay in the following simple considerations. A liquid which contains no lanthanides or actinides (unfilled inner-shell atoms) has no sharp-line atomic absorption spectrum. Any of the relatively long-lived nuclear states would have correspondingly narrow absorption lines. By shining light through a long tube containing a high concentration of the nuclear species of interest in a transparent liquid form, it might be possible to observe a fairly low-oscillator-strength nuclear transition. In fact a rough calculation shows that, with the high-dispersion grating available, and for the nuclide concentration feasible, an oscillator strength of 2×10^{-13} could be detected, which easily includes allowed nuclear magnetic dipole transitions.

The existence of the 27-minute isomer of U^{235} gives some encouragement to this project. This is an electric octupole transition having a broad energy spectrum with structure at 1/2 and 11 eV and end point at 23 eV. The energy structure thus includes the optical spectrum. The surprising aspect is that the "line" is not at all narrow as would be expected from its lifetime; such a structure would be difficult to discern from our experiment. In any event the possibility of observing this particular transition by our technique is negligible. The state is observed to go by electron conversion, i.e., the multipole field of the nucleus gives its energy to an electron directly. Since the energy involved is so small, the electron conversion must occur at one of the outermost shells, for instance, the P or Q shells. The systematics of the conversion coefficients, as calculated on a single particle model, are such that the electron conversion is preferred over gamma emission as decay energy becomes low and as multipole order becomes high. In fact the lifetime of this state indicates a conversion coefficient $\alpha = N_{\text{conv. elec's}}/N_2 = 10^{19}$. For E3 photon emission of 23 eV energy between the assigned angular momentum states the theoretical lifetime is 10^{15} years; thus a gamma absorption experiment is unfeasible.

However, it is quite plausible that if transitions of similar energy in other nuclides exist, they have not been observed. Optical absorption would be very small. Conversion electrons would probably have less energy than necessary for ionization. The flux of photons following nuclear de-excitation by electron conversion in ordinary nuclear experiments would be very small, $\sim 10^7$ photons/hr. (From the point of view of this laboratory the last sort of experiment might be interesting, if excited-state samples could be procured.)

Theoretically, opinions are as follows:

1. The lowest generally-occurring nuclei excitations are the collective-model rotations and vibrations of asymmetric nuclei. These venture as low as 10 keV. However, according to G. Scharff-Goldhaber, the theory of these excitations is satisfactory to predict that there will be no lower-lying excitations.

2. The many-particle theory of infinite nuclear matter comes up with energy gap predictions in the range of 1 keV. This should not be construed as support for the existence of low-lying levels; according to E.M. Henley, even confining the matter to a radius of 25 fermis raises this gap prediction to the usual energies.

3. The understanding of the U^{235m} state seems to be that two nuclear levels are crossing at that nuclide. The energy difference is considered a remarkable coincidence, representing superposition to one part in 10^5. Such superposition should be approached from the single particle point of view and if found elsewhere, might be expected away from closed shells in odd nuclei where nuclide systematics indicate level crossing. (The usual relations of this approach predict any transitions would be E2 or higher.) A possible alternative point of view is that this is a case of near-degeneracy or some kind of degeneracy split by some kind of interaction.

In these experiments, by considering the issues raised above and also questions of abundances, solubilities, densities, and transparencies, the following substances were selected:

Substance	Heavy Nuclides/cc	Band Examined	Stable Isotopes
B_1Cl_3 in HCl	4×10^{21}	5100 A° - 8900 A° (1.4 - 2.4 eV)	1
$Pb(C_2H_5)_4$	3×10^{21}		4
$H_g\ (CH_3)_2$	7×10^{21}	4000 A° - 9000 A° (1.4 - 3.1 eV)	7

Except for the rotational spectrum of O_2 (a substance present in the spectroscope) no narrow lines were observed for Bi^{209} or for the isotopes of mercury. The lead experiment was unsuccessful, as it turns out that this substance is photocatalyzed to an opaque oxide. Some other substances may be chosen for examination.